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Mesoscopic dynamics of copolymer melts: From density dynamics to external potential dynamics using nonlocal kinetic coupling

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In this paper we apply nonlocal kinetic coupling to the dynamic mean-field density functional method, which is derived from generalized time-dependent Ginzburg–Landau theory. The method is applied to the mesoscopic dynamics of copolymer melts, which was previously simulated using a local coupling approximation. We discuss the general theory of time evolution of density variables with general kinetic coefficients developed by Kawasaki and Sekimoto, and especially the limits of the theory that yield the local coupling approximation, the collective Rouse dynamics model, and the reptation dynamics model. We show how a simple approximation to the Rouse dynamics model leads to a feasible numerical model that includes the essential physical features of nonlocal kinetic coupling. This results in a dynamic equation for the external potential instead of the density which allows us to perform calculations of microphase separation in copolymer melts with increased relevance to experimental results. As may be expected from a numerical model that includes nonlocal kinetic coupling, the numerical results show an increased computational efficiency, less defects in the final morphology, and a faster increase of the order parameter compared to local kinetic coupling. © 1997 American Institute of Physics. [S0021-9606(97)50339-4]

I. INTRODUCTION

The dynamic mean-field density functional theory provides a numerical method for the calculation of polymer liquid morphology dynamics in 3-D.¹ The method is a modification of model B,^{2,3} i.e., a generalized time-dependent Ginzburg–Landau theory for conserved order parameter of the following general form:⁴

$$\begin{aligned} \frac{\partial \rho_I(\mathbf{r})}{\partial t} = & \sum_{j=1}^M \int_V \mathcal{D}_{IJ}(\mathbf{r}, \mathbf{r}_1) \mu_J(\mathbf{r}_1) d\mathbf{r}_1 \\ & - \beta^{-1} \sum_{j=1}^M \int_V \frac{\delta \mathcal{D}_{IJ}(\mathbf{r}, \mathbf{r}_1)}{\delta \rho_J(\mathbf{r}_1)} d\mathbf{r}_1 + \eta_I(\mathbf{r}, t), \\ \mathcal{D}_{IJ}(\mathbf{r}, \mathbf{r}_1) = & \nabla_{\mathbf{r}} \cdot \Lambda_{IJ}(\mathbf{r}, \mathbf{r}_1) \nabla_{\mathbf{r}_1} \end{aligned} \quad (1)$$

with particle concentration fields $\rho_I(\mathbf{r})$ ($I=1,\dots,M$), Onsager kinetic coefficients Λ_{IJ} , intrinsic chemical potentials $\mu_I \equiv \delta F / \delta \rho_I(\mathbf{r})$ (F is the free energy), $\beta^{-1} = k_B T$, and noise fields $\eta_I(\mathbf{r}, t)$. The noise has a Gaussian distribution with moments dictated by a fluctuation-dissipation theorem.^{4–6}

In Refs. 2, 3, and 7–12, and references cited therein, one can find numerous examples of computer simulations of time-dependent Ginzburg–Landau models for two- or three-component incompressible liquids with linear transport coefficients and relatively simple phenomenological models for the free energy. The goal of mesoscopic modeling is to obtain a theory of ordering phenomena in polymer liquids, based on a molecular description. We use a free-energy functional, derived for a collection of Gaussian chains in a mean-field environment. In this approach we try to retain as much as possible of the underlying molecular detail, i.e., the architecture and composition of the chain molecules are important. To this end, we do not use an expansion of the free

energy in the order parameters, as is commonly done in Ginzburg–Landau models, but rather use a single chain inverse density functional description for the chemical potentials. The chemical potential is split into an ideal part; the external potential resulting from Gaussian single chain statistics, and a nonideal part; the mean-field potential resulting from interchain interactions. The density (particle concentration) fields and external potential fields are coupled bijectively through the density functional. Previously, we studied the random term,⁴ the Gaussian chain density functional,¹³ and the relation with fourth-order expansions.¹⁴ Some results of numerical calculations of phase separation in *incompressible* block copolymer melts were discussed in Ref. 1. In Ref. 15 the method was extended to compressible polymer systems.

In this paper we improve upon the important assumption of a local exchange kinetic mechanism in the dynamic mean-field density functional method. The local exchange form for the Onsager kinetic coefficients was mainly used in Ref. 1 because of its simplicity and computational efficiency. The local form mimics the exchange effects in the nonlinear regime. However, the assumption of locality is not rigorously correct as is shown in a number of theoretical^{16–22} and experimental studies.^{23–26} The kinetic coefficient is predicted to have a decay-length of roughly the coil size in both the case of reptation^{27,28} and Rouse dynamics.^{18,22} In Refs. 23–25 the early state of spinodal decomposition is studied experimentally for various homopolymer blends by small angle neutron (SANS) or x-ray (SAXS) scattering, which allows observation of the dynamic structure factor. For large spatial frequencies the normalized Onsager coefficient behavior is found to be similar to predictions from Cahn–Hilliard–Cook (CHC) theory in the reptation regime.^{16–19,23,24,26} In Ref. 23

deviations from exponential behavior occur that are attributed to the measurement being close to the glass transition temperature. In Ref. 24 the range of the Onsager coefficient is found to be time dependent and increases to values larger than R_g , due to entanglement effects. The Onsager coefficient is studied over a wider range of spatial frequencies in Ref. 25; the results clearly demonstrate the q dependence of the coefficient, in semi-quantitative agreement with theoretical predictions. In Ref. 26, the Onsager coefficient is found to agree very well with predictions from Ref. 17 over a large frequency range, whereas the agreement to predictions from Refs. 28 and 29 is only found for very large frequencies. Several other authors have studied the ordering process of block (co)polymers using SANS or SAXS techniques,^{30–36} but only a few of them have made the connection to linearized CHC theory as explained in Refs. 16–18. In Ref. 31 no apparent q dependence is found for the Onsager coefficient, whereas in Ref. 32 a reasonable correspondence is found to estimated values for the Onsager coefficient that were extracted from CHC theory. It is argued in Ref. 34 that, in general, experimental results are hard to compare to (linearized) CHC theory because there are several severe theoretical limitations.

In the near future we intend to study the dynamic structure factor numerically and compare our results to the experiments mentioned above, especially with regard to the later stages of demixing where classical linear theory is not applicable. Since experimental results show that kinetic coupling is nonlocal, we require an efficient method to include nonlocal kinetic coupling in our computational algorithms; such a method is demonstrated in the present paper.

We employ the general dynamical theory of polymer melt morphology that was derived by Kawasaki and Sekimoto.^{27–29} The Kawasaki–Sekimoto derivation is based on a rigorous projection formalism and neglects elastic effects. For a detailed discussion of the projection formalism applied to collective concentration and stress variables, we refer to Ref. 37. By choosing different forms for the mobilities, the local coupling approximation, the collective Rouse dynamics model, and the reptation dynamics model can be derived.

The collective Rouse dynamics model has been described in detail,³⁸ but has to our knowledge never been used before in its full extent to describe phase-separation dynamics in inhomogeneous copolymer melts. We show how an approximation to the Rouse dynamics model leads to a feasible numerical model that avoids calculation of two-body correlators at every time step. The new model describes the dynamics of the external potential field instead of the density field and will be called the external potential dynamics (EPD) model. The new model possesses all the relevant features of nonlocal kinetic coupling, and can readily be applied to both homogeneous and inhomogeneous systems of any polymer composition. We have not yet succeeded in complementing the new model with an equally efficient algorithm for calculating the correlated Langevin noise. The Langevin noise should have a precise correlation, dictated by a fluctuation-dissipation theorem. In the new EPD model the

noise correlation is formally described by an inverse correlation function which is difficult to calculate numerically at the moment (see Sec. V). In the calculations we now use uncorrelated white noise sources. Despite this drawback, we believe that the new EPD model has great promise for the future and provides a first step toward increasing the relevance of our calculations to experimental results.

For demonstration purposes we tested the EPD model on the morphology dynamics in a diblock copolymer melt—this is a system we studied previously with a local kinetic coupling model.^{1,15} The results indicate that the nonlocal coupling is computationally more efficient and leads to faster morphology dynamics, compared with the earlier local coupling model. The overall features of the morphology on length scales larger than the coil size are conserved and the number of defects decreases as may be expected if nonlocal kinetic coupling effects are added to the dynamics model.

II. THEORY

A. Derivation of dynamic equations with nonlocal kinetic coupling

1. Mean-field density functional theory

We first recapitulate part of the dynamic mean-field density functional theory as explained in detail in Ref. 1.

We consider a melt of volume V , containing n Gaussian chains, each of length N . There are Z particle concentration fields $\rho_I(\mathbf{r})$ ($I = 1, \dots, Z$), Z external potentials $U_I(\mathbf{r})$, and Z intrinsic chemical potentials $\mu_I(\mathbf{r})$.

Imagine that on a coarse-grained time scale, there is a certain collective particle concentration field $\rho_I(\mathbf{r})$ of the beads (statistical units consisting of a fluctuating string of 5–15 monomers) of type I . Given this concentration field, a free-energy functional $F[\rho]$ is defined as follows:

$$F[\rho] = -\beta^{-1} n \ln \Phi + \beta^{-1} \ln n! - \sum_I \int U_I(\mathbf{r}) \rho_I(\mathbf{r}) d\mathbf{r} + F^{\text{nid}}[\rho]. \quad (2)$$

$F^{\text{nid}}[\rho]$ is the mean-field contribution from the nonideal interactions. Φ is the partition functional for the ideal Gaussian chains in the external field U_I given by

$$\Phi \equiv \text{Tr}_c e^{-\beta[H^G + \sum_{s=1}^N U_s(\mathbf{R}_s)]}, \quad (3)$$

where H^G is the Gaussian chain Hamiltonian

$$H^G = \frac{\beta^{-1} 3}{2a^2} \sum_{s=2}^N (\mathbf{R}_s - \mathbf{R}_{s-1})^2, \quad (4)$$

with a the Gaussian bond length parameter. The trace Tr_c is limited to the integration over the coordinates of one chain

$$\text{Tr}_c(\cdot) = \mathcal{N} \int_{V^N} (\cdot) \prod_{s=1}^N d\mathbf{R}_s. \quad (5)$$

\mathcal{N} is a normalization constant. The free-energy functional is derived from an optimization criterium¹ which introduces the external potential field U_I as a Lagrange multiplier field. The

relation between the external potentials and the concentration fields is bijective and given by a density functional for ideal Gaussian chains:

$$\rho_I[U](\mathbf{r}) = n \sum_{s'=1}^N \delta_{Is'}^K \text{Tr}_c \psi \delta(\mathbf{r} - \mathbf{R}_{s'}). \quad (6)$$

$\delta_{Is'}^K$ is a Kronecker delta function with value 1 if bead s' is of type I and 0 otherwise. ψ is the single chain configuration distribution function

$$\psi = \frac{1}{\Phi} e^{-\beta[H^G + \sum_{s=1}^N U_s(\mathbf{R}_s)]}. \quad (7)$$

The intrinsic chemical potentials μ_I are defined by the functional derivatives of the free energy:

$$\mu_I(\mathbf{r}) \equiv \frac{\delta F}{\delta \rho_I(\mathbf{r})} = -U_I(\mathbf{r}) + \frac{\delta F^{\text{nid}}}{\delta \rho_I(\mathbf{r})}. \quad (8)$$

Formally, the nonideal free energy can be split into two parts:

$$F^{\text{nid}}[\rho] = F^c[\rho] + F^e[\rho],$$

where F^e contains the excluded volume interactions, and F^c the cohesive interactions. In Ref. 15 we have discussed different models to account for the excluded volume interactions. In the present paper (cf. Ref. 15), we employ an idea which is originally from Helfand³⁹ for the nonideal free energy. The Helfand free energy is similar to

$$F^{\text{nid}}[\rho] = F^{c,\text{ex}}[\rho] + \frac{\kappa_H}{2} \int \left(\sum_I v_I \rho_I - \sum_I v_I \rho_{0I} \right)^2 d\mathbf{r}, \quad (9)$$

where κ_H is a compressibility parameter. $F^{c,\text{ex}}$ is the free energy resulting from the cohesive interactions, which contains the exchange parameters $\Delta\epsilon_{IJ}$ (with $\Delta\epsilon_{II}=0$ and $\Delta\epsilon_{IJ \neq I} \geq 0$) only. The intrinsic chemical potential is now given by

$$\begin{aligned} \mu_I(\mathbf{r}) = & -U_I(\mathbf{r}) + \sum_J \int_V \Delta\epsilon_{IJ}(|\mathbf{r} - \mathbf{r}'|) \rho_J(\mathbf{r}') d\mathbf{r}' \\ & + \kappa_H v_I \sum_J v_J \rho_J(\mathbf{r}). \end{aligned} \quad (10)$$

In general, a penalty function will allow small density fluctuations around the mean bulk density. In this approach, κ_H is a global constant, independent of composition, that can be related to experimental values of isothermal compressibility.⁴⁰

2. Equations for morphology dynamics

We study the dynamics equation

$$\frac{\partial \rho_I(\mathbf{r}, t)}{\partial t} = - \sum_J \int_V M_{IJ}(\mathbf{r}, \mathbf{r}') \mu_J(\mathbf{r}') d\mathbf{r}', \quad (11)$$

where

$$\begin{aligned} M_{IJ}(\mathbf{r}, \mathbf{r}') = & n \left\langle \frac{\partial \hat{\rho}_I}{\partial \mathbf{R}} \cdot \hat{\mathbf{M}} \cdot \frac{\partial \hat{\rho}_J}{\partial \mathbf{R}} \right\rangle \\ = & n \mathcal{N} \int_{V^N} \psi \left(\begin{array}{c} \frac{\partial}{\partial \mathbf{R}_1} \sum_{s=1}^N \delta_{Is}^K \delta(\mathbf{r} - \mathbf{R}_s) \\ \vdots \\ \frac{\partial}{\partial \mathbf{R}_N} \sum_{s=1}^N \delta_{Is}^K \delta(\mathbf{r} - \mathbf{R}_s) \end{array} \right) \\ & \cdot \left(\begin{array}{ccc} \hat{M}_{11} & \cdots & \hat{M}_{1N} \\ \vdots & & \vdots \\ \hat{M}_{N1} & \cdots & \hat{M}_{NN} \end{array} \right) \\ & \cdot \left(\begin{array}{c} \frac{\partial}{\partial \mathbf{R}_1} \sum_{s'=1}^N \delta_{Js'}^K \delta(\mathbf{r}' - \mathbf{R}_{s'}) \\ \vdots \\ \frac{\partial}{\partial \mathbf{R}_N} \sum_{s'=1}^N \delta_{Js'}^K \delta(\mathbf{r}' - \mathbf{R}_{s'}) \end{array} \right) d\mathbf{R}_1 \cdots d\mathbf{R}_N. \end{aligned} \quad (12)$$

$\langle \cdots \rangle = \text{Tr}_c \cdots \psi$ is the (normalized) ensemble average over the single chain distribution function ψ . Equation (12) is obtained from the general equation (2.20) in Kawasaki's and Sekimoto's first paper²⁷ by chainwise diagonalizing the master ensemble averaged mobility $\Lambda_{rr'}\{\rho(t)\}$ [Eq. (2.18) from Ref. 27]. In the following section we briefly recall the various chain dynamics regimes that determine the choice for the mobility coefficients $\hat{M}_{ss'}$.

The Langevin noise can be added formally by application of the fluctuation-dissipation theorem for collective fluctuations. For a brief discussion of the calculation issues we refer to Sec. V.

B. Approximations in different chain dynamics regimes

In the local coupling model $\hat{\mathbf{M}}$ is the identity matrix times a constant mobility $M_{\text{bead}} = \beta D_{\text{lca}}$, so that all nondiagonal terms $M_{s,s' \neq s}$ are zero. M_{bead} does not depend on the chain length N and the kinetic coupling between different beads is completely neglected. This is the approximation used in our previous papers^{1,4,13-15} and also in earlier estimates for the Onsager coefficient in Rouse dynamics.⁴¹ Many dynamic models based on Ginzburg–Landau-type free-energy functionals (Cahn–Hilliard, Flory–Huggins–de Gennes, or variants thereof for block copolymers) make use of even a simpler approximation in which the Onsager coefficient is assumed to be a constant (for references see Ref. 14).

The local coupling theory (using the instantaneous bare mobility matrix in Rouse dynamics as in Ref. 41) leads to a very simple expression for the collective dynamics (see below), but it must be stressed that this approximation is not physically consistent. A physically consistent model requires that the mobility matrix $\hat{\mathbf{M}}$ is a constant matrix $M\mathbf{1}$, such that

$M_{ss'} = M_{\text{chain}} = \beta D_{\text{ro}}$. In the Rouse model the total friction of a chain moving in an external force field scales with the chain length N ; hence we expect that $M_{\text{chain}} \sim N^{-1}$. Since we have coarse-grained time with respect to the internal chain correlation times, the details of the internal forces play no role whatsoever for the collective dynamics. Therefore *any* single chain model (Gaussian, freely jointed chain, etc.) must yield the same functional form for the Onsager coefficient.¹⁸ This is the regime of collective Rouse dynamics which was described in detail (for homogeneous systems) in Ref. 38.

The reptation regime is also relatively simple, since in this case the beads are constrained to move along the polymer tube axis. This regime is studied extensively in Refs. 28 and 29.

The various approximations lead to the following collective dynamics:

$$\frac{\partial \rho_I}{\partial t} = \beta D_{\text{lca}} \nabla_{\mathbf{r}} \cdot \rho_I(\mathbf{r}, t) \nabla_{\mathbf{r}} \mu_I(\mathbf{r}, t) \quad \text{local coupling,} \quad (13)$$

$$\frac{\partial \rho_I}{\partial t} = \beta D_{\text{ro}} \sum_{\mathbf{r}'} \nabla_{\mathbf{r}} \cdot P_{IJ}(\mathbf{r}, \mathbf{r}') \nabla_{\mathbf{r}'} \mu_J(\mathbf{r}') d\mathbf{r}' \quad \text{Rouse,} \quad (14)$$

$$\frac{\partial \rho_s}{\partial t} = -\beta D_c \int_V \int_0^N ds' \left[\frac{\partial^2}{\partial s \partial s'} P_{ss'}(\mathbf{r}, \mathbf{r}') \right] \mu_{s'}(\mathbf{r}') d\mathbf{r}' \quad \text{reptation.} \quad (15)$$

The reptation equation (15) is taken from Ref. 28 for a continuous chain; the other equations can be derived by insertion of $\hat{\mathbf{M}}$ in (11). The equation for local coupling dynamics is the same as we used before;¹ the general equation for collective Rouse dynamics (14) reduces to the equation for Rouse dynamics as given in Ref. 38 for homogeneous systems. D_c is the diffusion constant along the tube axis as defined in Ref. 28; the friction constant of reptative motion is given by $k_B T / D_c$. As is known from Refs. 17 and 38, $D_c \sim N^{-1}$. In Ref. 27 Kawasaki and Sekimoto have derived the general master equation for morphology dynamics (11). In Ref. 28 they have given a simpler derivation for reptation dynamics. In the Appendix we show that a similar derivation can be given for the collective Rouse dynamics model. $P_{ss'}$ and P_{IJ} are two-body correlators defined by (cf. Ref. 28):

$$P_{ss'}(\mathbf{r}, \mathbf{r}') \equiv n \langle \delta(\mathbf{r} - \mathbf{R}_s) \delta(\mathbf{r}' - \mathbf{R}_{s'}) \rangle, \quad (16)$$

$$P_{IJ}(\mathbf{r}, \mathbf{r}') \equiv \sum_{s=1}^N \sum_{s'=1}^N \delta_{Is}^K \delta_{Js'}^K P_{ss'}(\mathbf{r}, \mathbf{r}'). \quad (17)$$

In the homogeneous melt the two-body correlators $P_{IJ}(\mathbf{r}, \mathbf{r}')$ are given by $P_{IJ}^0(|\mathbf{r} - \mathbf{r}'|)$, with Fourier transform

$$P_{IJ}^0(q) = \frac{n}{V} \sum_{s=1}^N \sum_{s'=1}^N \delta_{Is}^K \delta_{Js'}^K \omega^{|s-s'|}, \quad (18)$$

$$\omega = e^{-a^2 q^2 / 6}. \quad (19)$$

As far as we know there has been no attempt to use the full equation for Rouse dynamics for inhomogeneous phase-separating systems due to the computational burden of calculating $P_{IJ}(\mathbf{r}, \mathbf{r}')$ at every time step. In the next section we show how a feasible numerical model can be derived that incorporates all important physical features of nonlocal kinetic coupling.

The dynamic equations are closed by the expression for the intrinsic chemical potential (8), which includes the highly nonlinear and nonlocal *inverse* density functional $U[\rho]$ [see Eq. (6)]. An explicit expression for the inverse density functional is not known, so that even in the simplest case of the local coupling model a general analytical solution for the dynamics is impossible to give.

We briefly recapitulate the limit of the homogeneous system for the different dynamics models. In case of weakly inhomogeneous polymer melts, relations for the Onsager coefficient can be derived by linearization in all models. Using translational invariance, and denoting $q = |\mathbf{q}|$, the dynamic equations in Fourier space are then given by

$$\frac{\partial \rho_I(q)}{\partial t} = -q^2 \sum_J \Lambda_{IJ}(q) \frac{\mu_J(q)}{kT}, \quad (20)$$

which defines the Onsager coefficient Λ_{IJ} . According to the three dynamic models, the Onsager coefficient for a homogeneous *homopolymer* melt is given by

$$\Lambda(q) = \begin{cases} D_{\text{lca}} \rho_0 & \text{local coupling} \\ D_{\text{ro}} \rho_0 N \frac{2(x + e^{-x} - 1)}{x^2} & \text{Rouse} \\ D_c \frac{a^2 \rho_0}{6} \frac{2(1 - e^{-x})}{x} & \text{reptation.} \end{cases} \quad (21)$$

Here, $x = Na^2 q^2 / 6$ and $\rho_0 = nN/V$ is the initial average density. The Debye function $(x + e^{-x} - 1)/x^2$ in the Onsager coefficient for Rouse dynamics applies to large chains where $N \gg 1$; for homopolymer chains of arbitrary length the geometric sum in Eq. (18) amounts to $\rho_0(2\omega^{N+1} - 2\omega^2 - 2N\omega + N + N\omega^2)/[N(\omega - 1)^2]$. The Onsager coefficient for the collective Rouse dynamics model is discussed in detail in Ref. 38. Notice that the reptation equation (15) reduces to

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= \int_0^N ds \frac{\partial \rho_s}{\partial t} \\ &= \frac{-D_c}{k_B T} \int \mu(\mathbf{r}') [P_{NN} - P_{0N} - P_{N0} + P_{00}](\mathbf{r}, \mathbf{r}') d\mathbf{r}' \end{aligned} \quad (22)$$

for a homopolymer. From the Onsager coefficients for the three dynamic models in a homogeneous homopolymer melt, we can conclude that, given a certain chemical potential gradient, the dynamics is essentially proportional to ρ_0 for both the local coupling approximation and the Rouse model. In the reptation regime, the change of the density is proportional to ρ_0/N and the dynamics is slower.

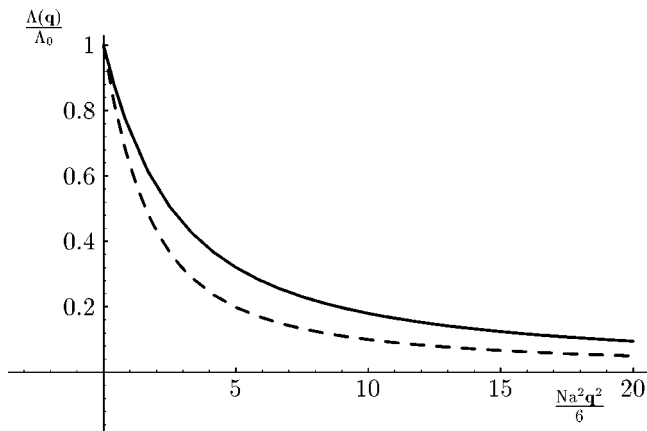


FIG. 1. Normalized Onsager coefficients $\Lambda(q)/\Lambda(0)$ in a homogeneous homopolymer melt for Rouse dynamics (—) and reptation dynamics (---) as a function of $Na^2q^2/6$.

The functional forms of Pincus¹⁷ and Kawasaki and Sekimoto^{21,28,29} for $\Lambda(q)$ in the reptation regime are the same. Binder¹⁸ and later Leibig and Fredrickson²² (who used the Kawasaki–Sekimoto expression) have found the same Onsager coefficient for Rouse dynamics as in Eq. (21). Binder argues that both for Rouse and reptation dynamics $\Lambda(q)$ is proportional to the Debye function, but this is not in agreement with our findings. However, the q dependencies of the two different nonlocal forms for reptation and Rouse dynamics do not differ very much, as can be seen from the normalized Onsager coefficients $\Lambda(q)/\Lambda(0)$ in Fig. 1. Almost all experimental results for q -dependent Onsager coefficients (see Sec. I) are compared to Cahn–Hilliard–Cook theory in the reptation regime. It would be interesting to make a systematic comparison to the theory for collective Rouse dynamics as well.

III. EXTERNAL POTENTIAL DYNAMICS MODEL

We will further study the collective Rouse dynamics model in order to derive a tractable numerical model for phase-separation dynamics. This will allow us to increase the relevance of our numerical calculations to experimental results which show that kinetic coupling is nonlocal instead of local. We have not yet found a way to cast the collective reptation dynamics in a similarly efficient numerical model. From a computational point of view, the equation for the collective Rouse dynamics as in Eq. (14) has a major drawback. It requires the renewed calculation of the correlators $P_{ss'}(\mathbf{r}, \mathbf{r}')$, which are N^2 six-dimensional functions, each time step. This procedure is computationally very intensive and requires more storage than is available on most contemporary computers.

Here, the objective is to derive an equation of motion for the auxiliary field U from the collective dynamics of the concentration field ρ . As we will make clear below, the additional approximations are modest, while the new model leads to an enormous reduction in computational costs compared to the full collective Rouse dynamics model and possesses the essential physical features of nonlocal kinetic cou-

pling. We use two important properties from density functional theory as summarized in the beginning of Sec. II: (i) The density functional $\rho[U]$ is bijective, which means that there also exists a bijective transformation of the dynamics between U and ρ space. Therefore we can select the space which is most convenient for calculations. (ii) Furthermore, the derivative of the density functional with respect to the external potential is the two-body correlator P_{IJ} , which is precisely the nonlocal transport coefficient in the dynamics equation:

$$\frac{\delta \rho_I(\mathbf{r})}{\delta U_I(\mathbf{r}')} \equiv -\beta P_{IJ}(\mathbf{r}, \mathbf{r}'). \quad (23)$$

The collective Rouse dynamics is transformed from ρ to U space by application of the chain rule:

$$\begin{aligned} \frac{\partial \rho_I(\mathbf{r}, t)}{\partial t} &= \sum_J \int \frac{\delta \rho_I(\mathbf{r}, t)}{\delta U_J(\mathbf{r}', t)} \frac{\partial U_J(\mathbf{r}', t)}{\partial t} d\mathbf{r}' \\ &= -\beta \sum_J \int P_{IJ}(\mathbf{r}, \mathbf{r}') \frac{\partial U_J(\mathbf{r}', t)}{\partial t} d\mathbf{r}'. \end{aligned} \quad (24)$$

Combining this result with Eq. (14) we find for the collective Rouse dynamics

$$\begin{aligned} \sum_J \int P_{IJ}(\mathbf{r}, \mathbf{r}') \frac{\partial U_J(\mathbf{r}', t)}{\partial t} d\mathbf{r}' \\ = -D_{ro} \sum_J \nabla_{\mathbf{r}} \cdot \int P_{IJ}(\mathbf{r}, \mathbf{r}') \nabla_{\mathbf{r}'} \mu_J(\mathbf{r}') d\mathbf{r}'. \end{aligned} \quad (25)$$

We can rewrite Eq. (25) in operator notation for all I as follows:

$$\mathbf{P} \frac{\partial \mathbf{U}}{\partial t} = -D_{ro} \nabla \cdot \mathbf{P} \nabla \boldsymbol{\mu}. \quad (26)$$

Here the elements \mathbf{P}_{IJ} of matrix \mathbf{P} are linear operators defined by

$$\mathbf{P}_{IJ}(\cdot) \equiv \int P_{IJ}(\mathbf{r}, \mathbf{r}') (\cdot) d\mathbf{r}'. \quad (27)$$

$\mathbf{U} \equiv \{U_1(\mathbf{r}), \dots, U_Z(\mathbf{r})\}^T$ and $\boldsymbol{\mu} \equiv \{\mu_1(\mathbf{r}), \dots, \mu_Z(\mathbf{r})\}^T$. The operator Eq. (26) is still exact. Since the correlator matrix \mathbf{P} occurs both on the left- and right-hand side of Eq. (26), essentially both the forces and the fluxes are transformed from U to ρ space. In the linear regime the operators ∇ and $\mathbf{P}\nabla$ commute for the dot inner product since the two-body correlators are translationally invariant, and Eq. (26) reduces to

$$\mathbf{P} \frac{\partial \mathbf{U}}{\partial t} = -D_{ro} \mathbf{P} \nabla^2 \boldsymbol{\mu}. \quad (28)$$

The entire relation can now be expressed in U space by applying the inverse operator \mathbf{P}^{-1} which exists since the ρ – U relationship is bijective. This results in

$$\frac{\partial \mathbf{U}}{\partial t} = -D_{ro} \nabla^2 \boldsymbol{\mu}. \quad (29)$$

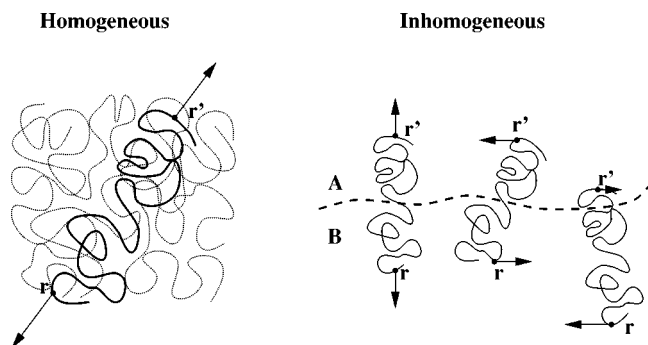


FIG. 2. Illustration of the gradients (indicated by arrows) $\nabla_{\mathbf{r}} P_{IJ}(\mathbf{r}, \mathbf{r}')$ and $\nabla_{\mathbf{r}'} P_{IJ}(\mathbf{r}, \mathbf{r}')$ in a homogeneous system (left figure) and an inhomogeneous system (right figure). In the inhomogeneous case two symmetric polymers (of which one is oriented perpendicular toward the interface) and one asymmetric polymer are indicated.

We can extend the application area of Eq. (29) to nonlinear regimes if we assume that the gradients of the two coordinates in the two-body correlators are opposite:

$$\nabla_{\mathbf{r}} P_{IJ}(\mathbf{r}, \mathbf{r}') = -\nabla_{\mathbf{r}'} P_{IJ}(\mathbf{r}, \mathbf{r}'). \quad (30)$$

Approximation (30) also results in Eq. (29), as can be most easily understood as follows. If we apply assumption (30), the right-hand side of Eq. (25) can be rewritten to:

$$\begin{aligned} \nabla_{\mathbf{r}} \cdot \int P_{IJ}(\mathbf{r}, \mathbf{r}') \nabla_{\mathbf{r}'} \mu_J(\mathbf{r}') d\mathbf{r}' \\ &= \int \nabla_{\mathbf{r}} P_{IJ}(\mathbf{r}, \mathbf{r}') \cdot \nabla_{\mathbf{r}'} \mu_J(\mathbf{r}') d\mathbf{r}' \\ &= - \int \nabla_{\mathbf{r}'} P_{IJ}(\mathbf{r}, \mathbf{r}') \cdot \nabla_{\mathbf{r}'} \mu_J(\mathbf{r}') d\mathbf{r}' \\ &= - \int \nabla_{\mathbf{r}'} \cdot P_{IJ}(\mathbf{r}, \mathbf{r}') \nabla_{\mathbf{r}'} \mu_J(\mathbf{r}') d\mathbf{r}' \\ &\quad + \int P_{IJ}(\mathbf{r}, \mathbf{r}') \nabla_{\mathbf{r}'}^2 \mu_J(\mathbf{r}') d\mathbf{r}' \\ &= \int P_{IJ}(\mathbf{r}, \mathbf{r}') \nabla_{\mathbf{r}'}^2 \mu_J(\mathbf{r}') d\mathbf{r}'. \end{aligned} \quad (31)$$

For the final step in this derivation we have applied the Gauss theorem and omitted the surface integral. Hence, approximation (30) also leads to Eq. (28) and thus to Eq. (29).

Figure 2 helps to understand the physics behind approximation (30). In a homogeneous phase the correlations only depend on the distance $|\mathbf{r} - \mathbf{r}'|$ due to the translational invariance and the gradients are exactly opposite. Therefore, approximation (30) is exact in the linear regime. In a (nonlinear) phase-separated system positions $(\mathbf{r}, \mathbf{r}')$ exist for which \mathbf{r} and \mathbf{r}' are in different phases. If neither \mathbf{r} nor \mathbf{r}' is in the interface, the gradients in Eq. (30) are always opposite (although they may differ in size, depending on the symmetry of the chain) and approximation (30) is justifiable.

Since the linear regime is automatically included as a limiting case, it is ensured that the proper Onsager coefficients for the homogeneous systems (21) are contained in the new model.

Precise estimates for the errors that are introduced by approximation (30) are not easy to give, except for some simple systems. For the collective diffusion of polymers of length $N=1$ (i.e., free monomers) $P_{11}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}')$, and the approximation amounts to replacing $\frac{1}{\rho} \nabla \cdot \rho \nabla \mu = \nabla^2 \mu + \nabla \ln \rho \cdot \nabla \mu$ by $\nabla^2 \mu$. This is quite reasonable in regions where concentration deviations relative to the homogeneous background are small ($\Delta \rho / \rho_0 < 1$), i.e., in regions away from interfaces.

In conclusion, we now arrive at the external potential dynamics (EPD) model:

$$\frac{\partial U_I}{\partial t} = -D_{\text{ro}} \nabla^2 \mu_I. \quad (32)$$

This is the desired equation of motion for the external potential field U , which replaces the equation of motion (14) for the density field ρ . Even though this model has a remarkably simple structure, it still possesses all the important features of nonlocal kinetic coupling. Notice that the Onsager coefficients are local and diagonal in U space. Hence, the kinetics is ideal in this space. This increases the speed of the numerical computations considerably because the cumbersome calculation of the correlators is not necessary. Although some problems remain with respect to the Langevin noise (see Sec. V), we believe that the external potential dynamics model is very useful to incorporate the effects of nonlocal kinetic coupling in mesoscopic dynamics algorithms, and will get us one step closer to correctly reproducing experimental results.

IV. ANALYSIS

In the following three examples we will employ linearization and perturbation analysis to gain further insight into the various dynamics models and to show that the Rouse dynamics model and especially the simplified EPD model exhibit the physical features of nonlocal kinetic coupling.

Incompressible melts. First consider the classical case of an incompressible blend of homopolymers A and B. Since the system is incompressible, a fluctuation in one of the concentration variables has to be compensated by an opposite fluctuation in the other variable. This introduces very special dynamic correlations. The collective Rouse dynamics is governed by two equations:

$$\frac{\partial \rho_A}{\partial t} = \beta D_{\text{ro}} \nabla \cdot \int P_{AA}(\mathbf{r}, \mathbf{r}') \nabla [\mu_A(\mathbf{r}') + \lambda(\mathbf{r}')] d\mathbf{r}', \quad (33)$$

$$\frac{\partial \rho_B}{\partial t} = \beta D_{\text{ro}} \nabla \cdot \int P_{BB}(\mathbf{r}, \mathbf{r}') \nabla [\mu_B(\mathbf{r}') + \lambda(\mathbf{r}')] d\mathbf{r}'. \quad (34)$$

Notice that the cross correlators P_{AB} and P_{BA} are zero in the single chain mean-field model. We have introduced an additional Lagrange parameter field λ in order to apply the incompressibility constraint:

$$\mathbf{J}_A + \mathbf{J}_B = 0. \quad (35)$$

Here, \mathbf{J}_I is the flux of component I , given by $\int P_{II}(\mathbf{r}, \mathbf{r}') \nabla[\mu_I(\mathbf{r}') + \lambda(\mathbf{r}')] d\mathbf{r}'$. For simplicity, we have assumed that the molecular volumes and individual friction coefficients of all beads are the same. The set of equations can be solved for λ (as in Refs. 16 and 28), which results in the exchange dynamics

$$\frac{\partial(\rho_A - \rho_B)}{\partial t} = 2\beta D_{\text{ro}} \nabla \cdot \int P(\mathbf{r}, \mathbf{r}') \nabla[\mu_A - \mu_B](\mathbf{r}') d\mathbf{r}', \quad (36)$$

$$\frac{\partial(\rho_A + \rho_B)}{\partial t} = 0. \quad (37)$$

Here $\rho_A - \rho_B$ is the order parameter, $\mu_A - \mu_B$ is the exchange chemical potential, and P is the exchange transport coefficient defined by

$$\begin{aligned} & \int P(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') d\mathbf{r}' \\ &= \int P_{AA}(\mathbf{r}, \mathbf{r}') [P_{AA} + P_{BB}]^{-1}(\mathbf{r}', \mathbf{r}'') \\ & \quad \times P_{BB}(\mathbf{r}'', \mathbf{r}''') f(\mathbf{r}''') d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}'''. \end{aligned} \quad (38)$$

It is obvious that in the general nonlinear case Eqs. (36) and (37) cannot be solved numerically. However, in the linear regime (36) reduces to a very simple equation. The Onsager coefficient for the diffusion of the order parameter [cf. Eq. (20)] is essentially proportional to the structure factor of the homogeneous ideal melt (as can easily be seen if the incompressibility constraint is applied in Fourier space):

$$\frac{2D_{\text{ro}}}{\Lambda(q)} = \frac{1}{P_{AA}^0} + \frac{1}{P_{BB}^0}. \quad (39)$$

By following a similar procedure, we find that the Onsager coefficient for the diffusion of the order parameter in a phase-separating *copolymer* melt is given by

$$\frac{2D_{\text{ro}}}{\Lambda(q)} = \frac{P_{AA}^0 + P_{AB}^0 + P_{BB}^0 + P_{BB}^0}{P_{AA}^0 P_{BB}^0 - P_{AB}^0 P_{BA}^0} = S_q^{0-1}, \quad (40)$$

where S_q^{0-1} is the inverse structure factor. Hence, expression (40) allows for direct comparison between our numerical calculations and experimental results. So far the analysis is traditional: the form of Eqs. (36) and (37) is the same as for incompressible reptation dynamics.²⁸ Notice however that the precise q dependence is different, see Eq. (21). We stress that the simplified EPD model yields exactly the same result, since in the linear regime the original collective Rouse dynamics model (21) and EPD model are identical.

At the moment it is not yet possible to directly use the exchange equations (36) and (37) for numerical calculations; the transport coefficients in the full Rouse model cannot be evaluated in any way. We have found that it is much more convenient to introduce a compressibility in the free-energy model, either by a well-chosen equation of state or a harmonic penalty function.^{39,15} Both models remove the instan-

aneous dynamic correlation imposed by the Lagrange parameter field λ . We will return to this topic in Sec. V.

Block copolymer interfaces. Next consider a segregated *A-B block* copolymer melt. Suppose that the system is initially in equilibrium in a state segregated strongly enough to exclude all *A*-type beads from the *B*-phase and all *B*-type beads from the *A*-phase. In that case, the probability that two *A*-type beads of a single chain are in separate phases is zero; $P_{AA}(\mathbf{r}_A, \mathbf{r}_B) = 0$ for all \mathbf{r}_A in the *A*-phase and all \mathbf{r}_B in the *B*-phase. Similarly, $P_{BB}(\mathbf{r}_A, \mathbf{r}_B) = 0$, $P_{AB}(\mathbf{r}_A, \mathbf{r}_B) \neq 0$ and $P_{BA}(\mathbf{r}_B, \mathbf{r}_A) \neq 0$. Since fluctuations can be passed from one phase to another by the two-body correlators P_{AB} and P_{BA} only, these terms control the interface dynamics both in the collective Rouse model and the reptation model.²⁹ Suppose that the chemical potential $\mu_A(\mathbf{r})$ of component *A* is perturbed by $\Delta\mu_A(\mathbf{r}) = \phi(\mathbf{r})$. In the original collective Rouse dynamics model (14) this results in a response of the concentration variables after a small time interval Δt of

$$\Delta\rho_A(\mathbf{r}_A) \propto \Delta t \nabla_{\mathbf{r}_A} \cdot \int P_{AA}(\mathbf{r}_A, \mathbf{r}'_A) \nabla_{\mathbf{r}'_A} \phi(\mathbf{r}'_A) d\mathbf{r}'_A, \quad (41)$$

$$\Delta\rho_B(\mathbf{r}_B) \propto \Delta t \nabla_{\mathbf{r}_B} \cdot \int P_{BA}(\mathbf{r}_B, \mathbf{r}'_A) \nabla_{\mathbf{r}'_A} \phi(\mathbf{r}'_A) d\mathbf{r}'_A, \quad (42)$$

while according to the simplified external potential dynamics model (28),

$$\Delta\rho_A(\mathbf{r}_A) \propto \Delta t \int P_{AA}(\mathbf{r}_A, \mathbf{r}'_A) \nabla_{\mathbf{r}'_A}^2 \phi(\mathbf{r}'_A) d\mathbf{r}'_A, \quad (43)$$

$$\Delta\rho_B(\mathbf{r}_B) \propto \Delta t \int P_{BA}(\mathbf{r}_B, \mathbf{r}'_A) \nabla_{\mathbf{r}'_A}^2 \phi(\mathbf{r}'_A) d\mathbf{r}'_A. \quad (44)$$

Since approximation (30) seems reasonable in the case of a strongly segregated block copolymer melt, Eqs. (41), (42), and (43), (44) are practically identical. Notice that the two-body correlators P_{IJ} are those of the inhomogeneous system. Hence, we expect that the interface dynamics is reproduced correctly in the EPD model.

Block copolymer melt near wall. Finally, consider a homogeneous block copolymer melt (above the microphase transition) which is suddenly brought into contact with a wall at time $t=0$. Such a situation arises when colloidal particles are dispersed in the melt, or when the melt is exposed to air or other fluids. We suppose that the *A* block adsorbs preferentially over the *B* block, such that an adsorption profile develops eventually. Equilibrium adsorption profiles for polymers adsorbed from solution have been calculated extensively by the Wageningen school using self-consistent field lattice models.⁴² In this case, the equilibrium profile is a decaying sinusoidal, with alternating *A* and *B* blocks. The ordering decreases toward the bulk and the *A* block is in contact with the surface. Similar profiles have been obtained using Monte Carlo and cluster growth probability models (see, e.g., Refs. 43–45). It is illustrative to see what the different dynamics models predict for the diffusion toward the surface. The equilibrium adsorption profiles for the different models are sketched in Fig. 3.

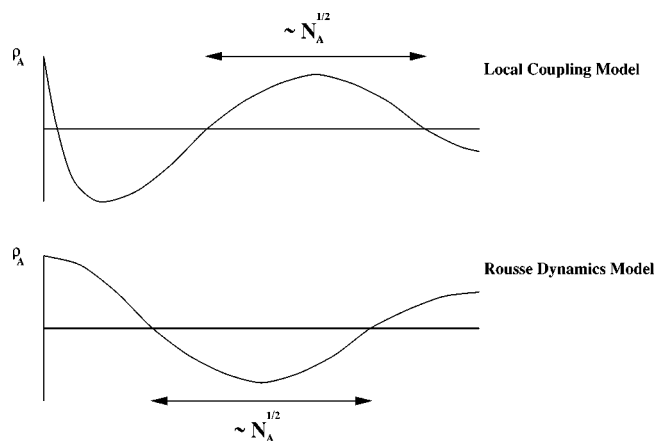


FIG. 3. Equilibrium adsorption profiles for a diblock copolymer melt near a wall in case of local coupling (upper figure) and Rouse dynamics (lower figure). The A block adsorbs preferentially.

First consider the local coupling model. A adsorbs rapidly to the surface and forms an adjacent depletion layer. Since the coupling is local, the *initial* depletion layer has a monomer length scale. Due to the decreased A concentration, the B concentration locally increases and starts to act as a barrier for further diffusion of A. The final state is metastable and consists of an A monomer layer and repeating blocks of B and A. We have performed some simulations in our group (using the local coupling model) that support this result (data not shown). Although the final profile is in equilibrium, it is not physically relevant; to our knowledge there are no experimental results of preferential adsorption where the adsorbed block forms a monomer size adsorption layer. The experiments always indicate that the first layer has a thickness of the order of the radius of gyration of the adsorbed block (see references in Ref. 42). Hence, we conclude that the local coupling model is not valid for interface problems.

Next consider the predictions of the collective Rouse dynamics model. This model incorporates nonlocal kinetic coupling on a polymer coil length scale. The immediate response of the A block has the same length scale. The depletion layer now starts at a distance $\sim aN^{1/2}$ away from the surface. The final profile is a decaying sinusoidal as expected, where the first layer is an A block of approximately the (block) coil size. Hence, the collective Rouse dynamics (and the simplified EPD variant) correctly predicts the physically relevant result.

V. NUMERICAL RESULTS AND DISCUSSION

We performed a numerical simulation, using EPD model (32) that incorporates nonlocal kinetic coupling. In our calculations, we neglect the higher-order contribution of the second (drift) term on the right-hand side of Eq. (1), which can even be proven to be zero for the simplest kinetic models. As we mentioned earlier, it is convenient to perform a compressible simulation. To make a comparison with previous simulation results, we have studied the compressible microphase separation dynamics in an A_8B_8 copolymer melt,

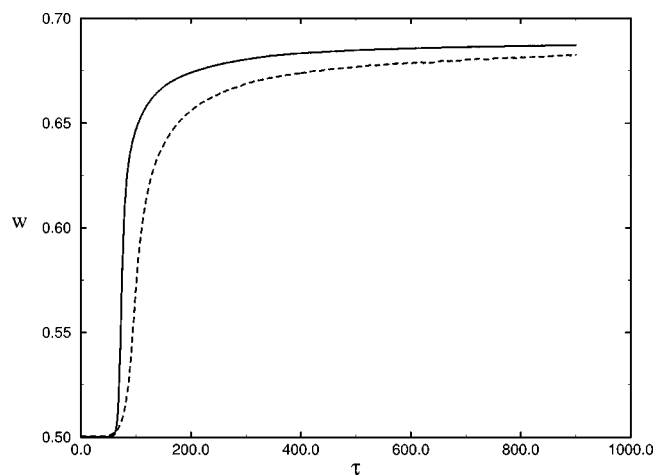


FIG. 4. Time evolution of volume-averaged order parameter w as a function of τ in a compressible A_8B_8 block copolymer melt (using Helfand's penalty model with $\kappa'_H=10$) for the local kinetic coupling model (-----) and the external potential dynamics model (—).

using Helfand's penalty model ($\kappa'_H=10$).¹⁵ The initial system is always homogeneous. Numerically, after discretizing the dynamic equations (32) on a grid, we use the following dimensionless Crank–Nicolson equations for each component I (for details see earlier papers^{1,15}):

$$(\beta U)_{Ir}^{k+1} - \frac{1}{2} \Delta \tau z_{Ir}^{k+1} = (\beta U)_{Ir}^k + (1 - \frac{1}{2}) \Delta \tau z_{Ir}^k + \eta_{Ir}^k. \quad (45)$$

Here, z_r^k denotes the discretized diffusion part at time level k and (cubic) grid position r

$$z_r = \sum_{\alpha} \sum_q d_{\alpha} [D_{\alpha} D_{\alpha}]_{rq} \beta \mu_{Iq}.$$

D_{α} is the discretized diffusion operator in grid direction α and μ_{Iq} is evaluated at grid position q . $\Delta \tau$ is a scaled time step ($\tau = D_{ro} h^2 t$ or $\tau = D_{lca} h^2 t$ where h is the grid size). The Crank–Nicolson equations are solved iteratively at every time step using a steepest descent method. The dimensionless variables for the time integration are the noise scaling parameter $\Omega = \nu^{-1} h^3 = 100$ (the number of beads per grid cell), $\Delta \tau = 0.5$, $\chi = 0.0$ or 1.0 (χ is the exchange parameter that accounts for the cohesive interactions as defined in Refs. 1 and 15), and $a/h = 1.15430$. η_{Ir}^k is the numerical noise. The actual (continuous) noise distribution for the EPD model

$$\frac{\partial U_I}{\partial t} = -D_{ro} \nabla^2 \mu_I + \eta_I, \quad (46)$$

according to the fluctuation-dissipation theorem, can be shown to be (in operator notation):

$$\langle \eta_I(\mathbf{r}, t) \rangle = 0, \quad (47)$$

$$\langle \eta_I(\mathbf{r}, t), \eta_J(\mathbf{r}', t') \rangle = -2\beta^{-2} D_{ro} \nabla_{\mathbf{r}}^2 P_{IJ}^{-1}(\mathbf{r}, \mathbf{r}') \delta(t - t'). \quad (48)$$

At the moment it is impossible to calculate the noise according to the above distribution for inhomogeneous melts. Therefore, we apply η_{Ir}^k with correlations according to local coupling kinetics. Although we realize that, in principle, we

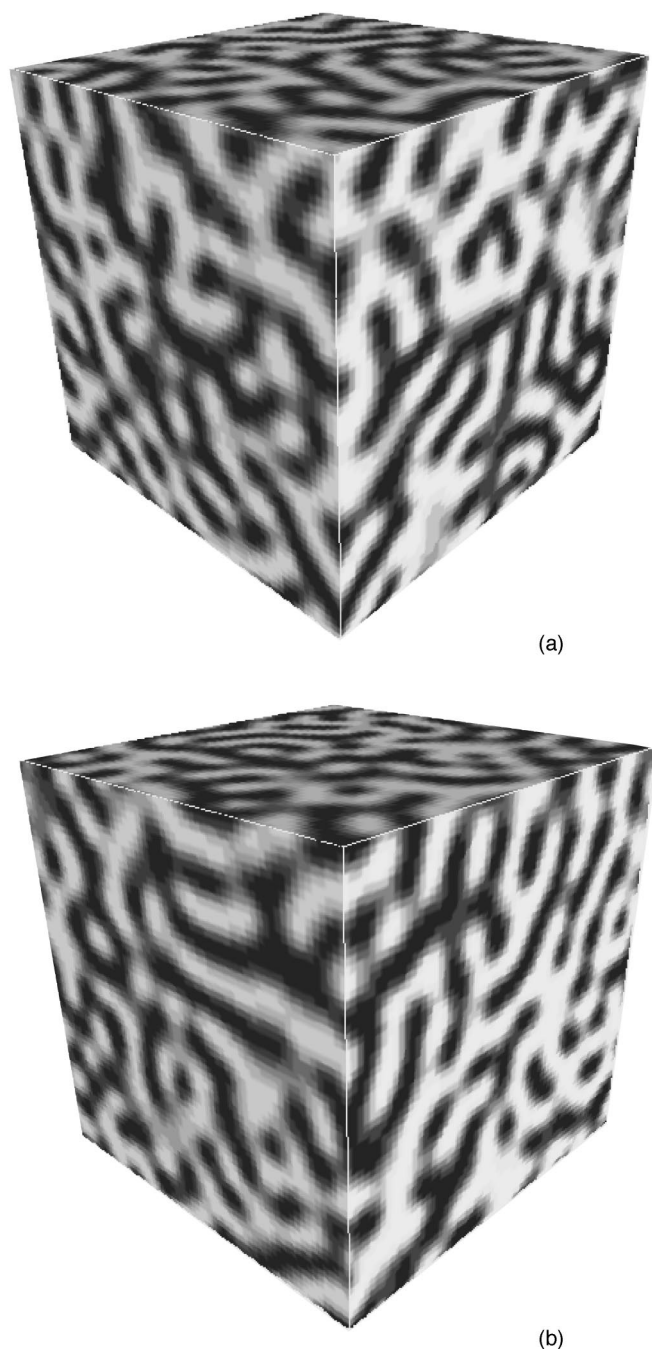


FIG. 5. Morphology of a compressible A_8B_8 block copolymer melt at $\tau = 800$ (using Helfand's penalty model with $\kappa'_H = 10$). The melt was quenched at $\tau = 50$ from $\chi = 0.0$ to $\chi = 1.0$. (a) Local kinetic coupling model. (b) External potential dynamics model.

violate the fluctuation-dissipation theorem, we argue that the influence of the noise is small due to the relatively large value of Ω . Notice that the noise is applied at every time step. We define an average measure of the order in the system by

$$\mathbf{w} \equiv \frac{1}{V} \int_V (\theta_A^2 + \theta_B^2) d\mathbf{r}. \quad (49)$$

Here, $\theta_I = \nu \rho_I$ is the dimensionless density field where ν is

the molecular volume. The effects of a change in order due to microphase separation and/or total density fluctuations are captured by \mathbf{w} . In Fig. 4 we plotted the time evolution of \mathbf{w} in a simulation using the local coupling approximation (all parameters as in Ref. 15) and the nonlocal coupling approximation in the Rouse dynamics regime. The phase separation was initiated with a quench from $\chi = 0$ to $\chi = 1.0$ at $\tau = 50$. We find that the simulation in the Rouse dynamics regime remains stable and that the order parameter increases faster shortly after the quench and stabilizes at a higher value than in the simulation that uses a local coupling approximation. The pictures of the simulation results indeed show larger structures and less defects (see Fig. 5) as may be expected if nonlocal kinetic coupling effects are included in the dynamics model. Because of the increased simulation times and the disappearance of defects, the influence of the periodic boundary conditions becomes apparent. We have made sure that all operators are discretized isotropically (see also Ref. 13), therefore the patterns do not show any preference for grid directions.

Since we use a Crank–Nicolson scheme, it is not so evident that this method should lead to increased computational efficiency, compared to the original density dynamics algorithms. However, we find in our numerical experiments that the nonlocal kinetic coupling algorithm requires less iterations to converge than the local kinetic coupling algorithm. We also performed some simulations using explicit integration schemes; they also remained stable and converged (data not shown).

VI. CONCLUSION

In this paper we have recapitulated some existing models for density dynamics that incorporate nonlocal kinetic coupling effects. A general model by Kawasaki and Sekimoto has been analyzed for different dynamics models (local coupling regime, Rouse dynamics regime, and reptation regime). The Rouse dynamics model cannot be used as such for numerical calculations, since it involves the repeated calculation of two-body correlators which is computationally too intensive. We have shown, however, how a simple approximation leads to a feasible numerical model that includes all important physical features of nonlocal kinetic coupling. We find that the new model describes the dynamics in terms of the external potential instead of the density. This model has been used to study the effects of nonlocal kinetic coupling on numerical simulations of compressible copolymer liquids using the dynamic mean-field density functional method. So far, we have not yet succeeded in implementing the noise according to the fluctuation-dissipation theorem for the external potential dynamics. However, we found that we can use noise that is distributed according to local coupling dynamics [and even (small) white noise] for practical calculations.

We find that compared to earlier simulations that only took local coupling effects into account, the nonlocal coupling effects cause the system to form less defects and larger structures. The order parameter increases faster and the final

ordering of the melt is increased with respect to local coupling simulations. Hence, the external potential dynamics model allows us to perform calculations of microphase separation in copolymer melts with increased relevance to experimental results. Incorporating nonlocal coupling effects also leads to an increase in computational efficiency, due to faster numerical convergence in the time integration methods.

In conclusion, we have succeeded in incorporating *non-local* coupling effects, based on the Rouse dynamics model into our simulations. We have not only improved the physical relevance of our mesoscopic simulations in this way, but have also found a very simple numerical model for external potential dynamics that leads to improved computational efficiency.

APPENDIX: DERIVATION COLLECTIVE ROUSE DYNAMICS MODEL

In this section we present a simple derivation of the collective Rouse dynamics model (14), along the lines set out for reptation dynamics in the second paper by Kawasaki and Sekimoto.²⁸ Suppose a polymer chain is under the influence of an external force field \mathbf{f}_s , where the force may be different for each bead s . The total force equals $\sum_{s=1}^N \mathbf{f}_s$. In the Rouse regime the correlations due to internal forces relax (much) faster than the coarse-grained collective dynamics. Hence, after a certain time that is much larger than the internal relaxation time, the chain will drift with a constant velocity $\mathbf{v}_{\text{drift}}$, according to (cf. Eq. 5.6 in Ref. 46)

$$\mathbf{v}_{\text{drift}} = \frac{M_0}{N} \sum_{s=1}^N \mathbf{f}_s.$$

Here we have assumed that the total friction is linear in N ; there is no hydrodynamic interaction between the beads and the solvent flows freely through the polymer coil. It is important to realize that *all* beads have the same systematic velocity on average.

Next we define the microscopic density variable

$$\hat{\rho}_s(\mathbf{r}) \equiv \delta(\mathbf{r} - \mathbf{R}_s).$$

By application of the chain rule, the microscopic analog of the equation of continuity is

$$\frac{\partial \hat{\rho}_s(\mathbf{r})}{\partial t} = -\nabla_{\mathbf{r}} \cdot \delta(\mathbf{r} - \mathbf{R}_s) \frac{\partial \mathbf{R}_s}{\partial t}.$$

Given the external force field \mathbf{f}_s , we replace the velocity $\partial \mathbf{R}_s / \partial t$ by the drift velocity $\mathbf{v}_{\text{drift}}$ for the entire chain (this is a valid procedure for the Rouse regime), and we obtain

$$\frac{\partial \hat{\rho}_s(\mathbf{r})}{\partial t} = -\frac{M_0}{N} \nabla_{\mathbf{r}} \cdot \delta(\mathbf{r} - \mathbf{R}_s) \sum_{s'=1}^N \mathbf{f}_{s'}(\mathbf{R}_{s'}).$$

In the thermodynamic limit, the microscopic variables can be replaced by collective variables (cf. Eq. 2.11 in Ref. 28)

$$\hat{\rho}_s(\mathbf{r}) \rightarrow \langle \hat{\rho}_s(\mathbf{r}) \rangle = \rho_s(\mathbf{r}) = \mathcal{N} \int_{V^N} \psi \hat{\rho}_s(\mathbf{r}) d\mathbf{R}_1 \cdots d\mathbf{R}_N,$$

which leads to

$$\begin{aligned} \frac{\partial \rho_s(\mathbf{r})}{\partial t} &= -\frac{M_0 \mathcal{N}}{N} \nabla_{\mathbf{r}} \cdot \int_{V^N} \psi \delta(\mathbf{r} - \mathbf{R}_s) \\ &\quad \times \sum_{s'=1}^N \mathbf{f}_{s'}(\mathbf{R}_{s'}) d\mathbf{R}_1 \cdots d\mathbf{R}_N. \end{aligned}$$

Similarly, in the thermodynamic limit, the external force field \mathbf{f}_s can be replaced by minus the gradient of the chemical potential (cf. Eq. 2.11 in Ref. 28) which results in

$$\begin{aligned} \frac{\partial \rho_s(\mathbf{r})}{\partial t} &= \frac{M_0 \mathcal{N}}{N} \nabla_{\mathbf{r}} \cdot \int_{V^N} \psi \delta(\mathbf{r} - \mathbf{R}_s) \\ &\quad \times \sum_{s'=1}^N \frac{\partial \mu_{s'}(\mathbf{R}_{s'})}{\partial \mathbf{R}_{s'}} d\mathbf{R}_1 \cdots d\mathbf{R}_N. \end{aligned}$$

The concentration of I -type particles is given in (6) by

$$\rho_I(\mathbf{r}) = n \left\langle \sum_{s=1}^N \delta_{Is}^K \hat{\rho}_s(\mathbf{r}) \right\rangle. \quad (\text{A1})$$

Therefore

$$\begin{aligned} \frac{\partial \rho_I(\mathbf{r}, t)}{\partial t} &= n \sum_{s=1}^N \delta_{Is}^K \left\langle \frac{\partial \hat{\rho}_s(\mathbf{r})}{\partial t} \right\rangle \\ &= n \sum_{s=1}^N \delta_{Is}^K \frac{\partial \rho_s(\mathbf{r})}{\partial t} \\ &= n \sum_{s=1}^N \delta_{Is}^K \frac{M_0 \mathcal{N}}{N} \nabla_{\mathbf{r}} \cdot \int_{V^N} \psi \delta(\mathbf{r} - \mathbf{R}_s) \\ &\quad \times \sum_{s'=1}^N \frac{\partial \mu_{s'}(\mathbf{R}_{s'})}{\partial \mathbf{R}_{s'}} d\mathbf{R}_1 \cdots d\mathbf{R}_N. \end{aligned} \quad (\text{A2})$$

Notice that a derivative with respect to a 3D coordinate should be interpreted as a gradient operator. We use the identities

$$\sum_J \sum_{s'=1}^N \delta_{Js'}^K \frac{\partial \mu_J(\mathbf{R}_{s'})}{\partial \mathbf{R}_{s'}} = \sum_{s'=1}^N \frac{\partial \mu_{s'}(\mathbf{R}_{s'})}{\partial \mathbf{R}_{s'}} \quad (\text{A3})$$

and

$$\int \delta(\mathbf{r}' - \mathbf{R}_{s'}) f(\mathbf{r}') d\mathbf{r}' = f(\mathbf{R}_{s'}) \quad (\text{A4})$$

to rewrite (A2) to

$$\begin{aligned} \frac{\partial \rho_I(\mathbf{r}, t)}{\partial t} &= n \sum_{s=1}^N \delta_{Is}^K \frac{M_0 \mathcal{N}}{N} \nabla_{\mathbf{r}} \cdot \int_{V^N} \psi \delta(\mathbf{r} - \mathbf{R}_s) \\ &\quad \times \sum_{s'=1}^N \sum_J \delta_{Js'}^K \frac{\partial \mu_J(\mathbf{R}_{s'})}{\partial \mathbf{R}_{s'}} d\mathbf{R}_1 \cdots d\mathbf{R}_N \\ &= n \sum_{s=1}^N \delta_{Is}^K \frac{M_0 \mathcal{N}}{N} \nabla_{\mathbf{r}} \cdot \int_{V^N} \int_V \psi \delta(\mathbf{r} - \mathbf{R}_s) \\ &\quad \times \sum_{s'=1}^N \sum_J \delta_{Js'}^K \delta(\mathbf{r}' - \mathbf{R}_{s'}) \end{aligned}$$

$$\begin{aligned}
& \times \nabla_{\mathbf{r}'} \mu_J(\mathbf{r}') d\mathbf{r}' d\mathbf{R}_1 \dots d\mathbf{R}_N \\
& = \frac{M_0}{N} \sum_J \nabla_{\mathbf{r}} \cdot \int_V n \sum_{s=1}^N \sum_{s'=1}^N \delta_{Is}^K \delta_{Js'}^K \\
& \quad \times \langle \delta(\mathbf{r} - \mathbf{R}_s) \delta(\mathbf{r}' - \mathbf{R}_{s'}) \rangle \nabla_{\mathbf{r}'} \mu_J(\mathbf{r}') d\mathbf{r}' \\
& = \frac{M_0}{N} \sum_J \nabla_{\mathbf{r}} \cdot \int_V P_{IJ}(\mathbf{r}, \mathbf{r}') \nabla_{\mathbf{r}'} \mu_J(\mathbf{r}') d\mathbf{r}'.
\end{aligned}$$

Here we have employed the definition for the two-body correlator $P_{IJ}(\mathbf{r}, \mathbf{r}')$ as given in Eq. (17). Since $M_0/N = \beta D_{\text{ro}}$, this result is exactly the same as the expression for collective Rouse dynamics in Eq. (14).

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